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Ab Initio Surface Core-Level Shifts and Surface Segregation Energies

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We have calculated the surface core-level energy shifts of the 4*d* and 5*d* transition metals by means of local-density theory and a Green's-function technique based on the linear muffin-tin orbitals method. Final-state effects are included by treating the core-ionized atom as an impurity located in the bulk and at the surface, respectively. It is shown that the study of surface core-level shifts provides an ideal tool for an accurate determination of the surface segregation energy of a substitutional $(Z+1)$ impurity in a Z metal host (Z denotes atomic number).

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The determination of surface core-level shifts (SCLS) provides valuable information that may be used to study fundamental surface issues such as surface electronic structure, surface structure, reconstruction, surface defects, surface energies, surface segregation, and adsorbate interaction [1]. Since 1978, when it was first shown [2] that this quantity could be detected experimentally, the measurements on transition metals have been restricted mainly to the 5*d* series [3,4]. However, recently the experimental technique has been developed to a point which allows determination of SCLS also for the 4*d* transition metals [5], thus broadening the range of materials that may be studied.

The first theoretical calculations of SCLS were based on a model derived from the theory of the shift in the core-level binding energy between the free atom and the metallic phase [6–8]. The calculations required the knowledge of a series of independent experimental data and allowed the determination of the SCLS for a large number of elements. A most important aspect of this work [7, 9] was the fact that it related the SCLS directly to the surface segregation energy for a substitutional $(Z+1)$ impurity in a metal of atomic number Z.

In a series of *ab initio* calculations [10, 11] the SCLS was derived from the difference in the relevant core-level energy eigenvalue of an atom at the surface and in the bulk. Hence, only inital-state effects were considered, and the fact that the agreement between theory and experiment has generally been unsatisfactory [12] is believed to be due to the neglect of final-state screening of the core hole [13]. At present *ab initio* calculations which include both initial- and final-state effects are still missing and it is the purpose of this Letter to present such theoretical data. From a materials science point of view the most important aspect of such calculations stems from the fact that the SCLS can be directly related to the surface segregation energy of substitutional impurities. As we shall demonstrate, theory is now sufficiently advanced to provide accurate data for this fundamental materials parameter which may otherwise only be determined with large uncertainties.

The SCLS is defined as the shift in the core-level binding energy for a surface atom relative to that of a bulk atom. The basic assumption in the theoretical approach presented by Johansson and Mårtensson [7] is that for a metal the symmetric part of the line profile for the core level corresponds to an electronically completely screened final state, i.e., a state in which the conduction electrons have attained a fully relaxed configuration in the presence of the core hole. In this picture, the core-level binding energy may therefore be expressed as the difference between the total energy of the relaxed final state and the initial unperturbed state. The support for the final-state screening picture comes from highly successful calculations of chemical core-level shifts using independent thermodynamic data [7].

In Fig. 1 we illustrate the core-level binding energy for a bulk and a surface atom, respectively. From this we arrive at a pictorial representation of the surface core-level shift, which immediately shows that the SCLS is equiva-

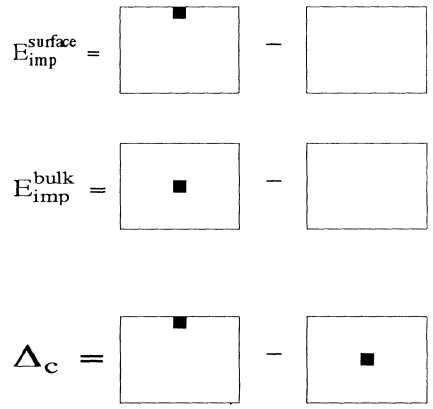

FIG. 1. Pictorial representation of the surface core-level shift. The filled square denotes a fully screened core hole, which is the final state of the core-ionized atom. The core-level binding energy is the total energy difference between the final state and the unperturbed initial state of the system. This is illustrated for a surface atom and for a bulk atom at the top and the middle of figure, respectively. The difference between them gives the surface core-level shift, as illustrated at the bottom of the figure.

lent to the surface segregation energy of the core-ionized atom. If the $(Z+1)$ approximation is used for the core-ionized atom, with atomic number Z, and if the impurity aspect of the excited atom is neglected, the SCLS Δ_c may be estimated from the simple expression [7, 9]

$$\Delta_c \approx E_S^{Z+1} - E_S^Z, \quad (1)$$

i.e., as the difference in surface energy E_S between the $(Z+1)$ and (Z) metallic elements. Using the familiar *empirical* relation $E_S \approx 0.2E_{\rm coh}$, where $E_{\rm coh}$ is the cohesive energy, (1) becomes

$$\Delta_c \approx 0.2(E_{\rm coh}^{Z+1} - E_{\rm coh}^Z). \quad (2)$$

The variation of the experimental SCLS across the $5d$ transition series is found to be in rather good agreement with the simple expression (2) [7] despite the fact that Re exhibits an anomalous SCLS when compared with the values for the neighboring elements W and Os [3]. Rather surprisingly Eq. (2) appears to reproduce this feature when experimental data for the cohesive energies are inserted into the expression. Now, the cohesive energy is defined as the energy gained in the transformation of a free atom into a bulk atom. It therefore invokes the free atomic state, whereas the SCLS involves only condensed atoms in different environments. Total energy electronic-structure calculations have revealed [14] that the somewhat anomalous cohesive energy for Re is of an atomic origin; i.e., it is an artifact of the atomic contribution to the cohesive energy, and will disappear if the cohesive energies are defined in terms of the same type of $d^n s^1$ muliplet average atomic state for all the $5d$ elements. This means in particular that the anomalous SCLS for Re cannot be explained by (2). In addition, it is clear that (2) is of limited value since, for example, it provides no information about the structural dependence of the surface shift.

Here we report *ab initio* calculations of the SCLS for the $4d$ and $5d$ transition metals which include final-state effects by treating a core-ionized atom as an impurity located in the bulk and at the surface. A related approach based on a film-geometry Green's-function technique has recently been applied to the case of the simple metal Al [15]. The present bulk and surface impurity calculations are performed by means of the Green's-function technique [16] based on the scalar-relativistic linear muffin-tin orbitals method [17, 18] within the tight-binding [19, 20], frozen core, and atomic-sphere approximations together with the local-density approximation in the Vosko-Wilk-Nusair parametrization [21]. The technique takes proper account of the broken translational symmetry perpendicular to the surface and has recently been used in extensive studies of work functions [22], surface energies [23], surface and interface magnetism [24, 25], and stacking fault energies in elemental metals [26]. The impurity aspect of the Green's-function technique is based on the original formulation by Gunnarsson *et al.* [27] which has been used successfully for point defects in silicon [28].

In the present approach the surface core-level shift is obtained by means of separate impurity calculations in the bulk and at the surface, the impurity being a core-ionized atom with one electron missing in the $3d$ shell for the $4d$ metals and in the $4f$ shell for the $5d$ metals. The bulk impurity calculation is based on the self-consistent Green's function for the perfect crystal and yields the impurity-solution energy $E_{\rm imp}^{\rm bulk}$. The surface impurity calculation is based on the self-consistent surface Green's function and yields the surface-impurity-solution energy $E_{\rm imp}^{\rm surface}$ whereby the SCLS may be obtained as the surface segregation energy of the impurity (cf. Fig. 1), i.e.,

$$\Delta_c = E_{\rm imp}^{\rm surface} - E_{\rm imp}^{\rm bulk}. \quad (3)$$

In the calculation of the total energies involved in (3) the sums of the one-electron energies are obtained from the generalized phase shifts as suggested by Gunnarsson *et al.* [27]. Hence, it is sufficient to include only four shells of nearest neighbors in the impurity calculations to obtain SCLS's which are converged in shell number to within ± 0.02 eV.

The results for the most close-packed surface of the observed crystal structures of the $5d$ transition metals are presented in the top panel of Fig. 2. It is seen that the present *ab initio* calculation gives a qualitatively correct description of the variation with atomic number in the measured SCLS's from Yb to Pt [3, 4]. It is furthermore seen that in most cases where experimental single-crystal data exist (squares), we obtain a complete quantitative agreement with experiment. Now, our calculated SCLS are indirectly related to the surface energy of the element (Z) at hand and that of its neighbor $(Z+1)$ while for estimates based on (1) this dependence is direct. The

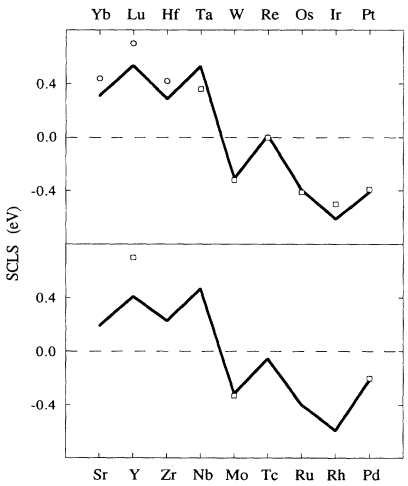

FIG. 2. Comparison between the calculated (thick lines) and the measured SCLS's for the $5d$ and $4d$ metals. The calculations refer to the most close-packed facets of experimentally observed crystal structures, i.e., fcc (111), bcc (110), or hcp (0001). The corresponding single-crystal experimental data are marked with squares. The circles for Yb-Hf refer to measurements made on polycrystalline samples.

discrepancy between theory and experiment [4] for bcc Ta may thus be traced back to the fact that the calculated surface energy of Ta appears to be underestimated by the present type of calculation [23]. The same effect, but smaller and of opposite sign, appears for fcc Ir. For the elements Yb-Hf the experimental SCLS's were obtained on polycrystalline samples and should not be compared directly with our calculated single-crystal values. It is, however, clearly seen that the measured trend for these elements is reproduced by our present results. Moreover, a lowering of the SCLS is to be expected when going from a polycrystalline sample to a close-packed well-defined surface, implying that the systematic difference between the experimental and theoretical data for Yb-Hf is caused by structural effects.

The fact that the SCLS changes sign through the series can be traced back to the screening properties. For all the transition metals the screening charge consists mainly of an extra d electron located around the core-ionized atom. For an early transition metal this screening electron enters the bonding part of the d band. Thus there is an additional bonding in the final state as compared to the initial state. Because of the decreased coordination number at the surface, both the initial and final states are less bonded for a surface atom than for a bulk atom. Since the final state is associated with more bonding than the initial state, the decrease of bonding at the surface affects the final state more than it does the initial state. Thus clearly the core-level binding energy will be larger at the surface than in the bulk and therefore the SCLS is positive. For a late transition metal the screening will take place in the antibonding part of the d band. Thus there is less bonding associated with the final state than with the initial state. This situation is just the opposite to the case for an early transition metal, hence a negative SCLS.

For a rectangular d density of states, which simulates especially the fcc phase fairly well, the bonding is $E_{\mathrm{bond}} = 1/2(n - n^2/10)W$ (W denotes bandwidth and n denotes number of d electrons). The bonding difference between the final and initial states is then $E_{\mathrm{bond}}(n+1) - E_{\mathrm{bond}}(n) \approx dE_{\mathrm{bond}}(n)/dn = (1-n/5)W/2$. In the beginning and at the end of the series, using a bandwidth of 5 eV, this difference has a magnitude of 2.5 eV. With a 20% reduction of the bonding at the surface, due to band narrowing, the difference between the bulk and the surface becomes 0.5 eV, which is the observed order of magnitude for SCLS.

The results for the $4d$ transition metals are presented in the lower panel of Fig. 2, where again the calculated data refer to the most close-packed surface of the observed crystal structures. For these elements there are only a few experimental values owing to the well-known difficulty of resolving the somewhat broader line shapes associated with the $3d$ core levels in this series. From the present theory, however, it is seen that the behavior across the series essentially follows that of the $5d$ series. In particular, the relative minimum for bcc Mo and maximum for hcp Tc are completely analogous to the values for the corresponding $5d$ elements. The SCLS for the hcp (0001) facet of Y is measured to be 0.7–0.9 eV [5], which is unusually large in comparison with both the calculated value and the value for the corresponding $5d$ metal. In contrast, the measured SCLS for the single-crystal (110) surface of bcc Mo and (111) surface of fcc Pd [5] are in complete quantitative agreement with the present results. This implies that our theoretical predictions for the neighboring elements should be highly reliable.

To investigate the crystal structure dependence of the SCLS we present in Fig. 3 the results of three series of calculations where the $5d$ elements are assumed to exhibit the most close-packed surface facets of the fcc, bcc, and hcp crystal structures. For the fcc 111 and the hcp 0001 facets the SCLS's of the elements Lu to Ir decrease almost linearly with d-band filling. This may be understood in terms of (1) because the surface energies of the fcc 111 and hcp 0001 facets are close to being parabolic [23]. Also the simple argument above for the rectangular band gave a linear dependence through the series for the SCLS.

The bcc SCLS's show stronger irregularities through the $5d$ series, which reflects the richer structure of the density of states for the bcc phase, causing, e.g., a less smooth surface energy variation through a d series. Thus the well-known two-peak structure of the d-band state density implies that the screening charge for bcc W and bcc Re has to be accommodated in an energy range with a low d density of states. This is energetically unfavorable for the bonding in the final state. Hence these two elements show large negative SCLS for the bcc phase. For tungsten, the calculated bcc SCLS is $\sim$ 0.35 eV lower than for the fcc phase, so that the anomalously low value in Fig. 2 is a structural effect. The difference between hcp and bcc Re is even larger. Since there is a structural change between W and Re from bcc to hcp the pronounced positive change in SCLS which appears between the two elements is again purely a structural effect [29].

To provide a critical examination of the commonly

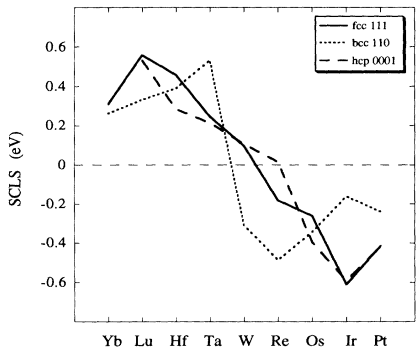

FIG. 3. Comparison between the calculated SCLS of the most close-packed surface of the fcc (line), bcc (dots), and hcp (broken line) crystal structures.

used $(Z+1)$ approximation we subject fcc Yb, bcc W, and fcc Pt to SCLS calculations for all core levels, and also substitute the core-ionized impurity with the $(Z+1)$ atom. For Yb and Pt we found that the different core holes and $(Z+1)$ replacement yield the same segregation energy to within 0.01 eV. For W(110) the spread is larger, 0.1 eV, so that the shifts for the $(Z+1)$ atom and the deeper core levels are less negative than that of the $4f$ level. The results for the other elements interpolate well between these findings, and in consistency with obtained results for the so-called initial-state shifts [11] we conclude that the equivalent core approximation is less valid for elements in the middle of a transition series than for the early and late elements. Thus for early and late transition metals the measured SCLS can be used as accurate surface segregation energies for substitutional $(Z+1)$ impurities in a Z metal host. For the other elements accurate values can be obtained by means of calculated corrections to the shifts.

In summary, we have presented a comprehensive series of calculations for SCLS's where the final-state screening effects have been invoked from first principles. The main goal has been to develop an efficient bulk-surface Green's-function technique for treating an impurity either in the bulk or at the surface. The method is thus well suited for general surface segregation studies, and such work is under progress. Because of the vertical nature of the x-ray excitation process no lattice relaxations are involved, greatly simplifying the theoretical treatment of SCLS. In most cases where SCLS measurements on single-crystal samples have been reported, these are fully reproduced by the present calculations. This demonstrates the validity of the final-state screening picture. The rapid change in SCLS in the neighborhood of hcp Re and hcp Tc is a consequence of the strong structural dependencies of the SCLS in the middle of a transition series.

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